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# DISTRIBUTION OF Pb AND Zn AND THEIR CHEMICAL SPECIEISATIONS IN THE PADDY SOILS FROM THE KOČANI FIELD (MACEDONIA)

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A b s t r a c t: The distribution and chemical specifications of Pb and Zn in the paddy soils of Kočani Field, Macedonia, were investigated using a sequential extraction procedure. This study was carried out in order to develop an understanding of the metal contamination found in the area which is due to historical and recent mining operations around Kočani Field. The paddy soil sample from location VII–2 in the vicinity of Zletovo mine in the western part of Kočani Field was found to contain highly elevated concentrations of Pb and Zn which are under reduction conditions very unstable and mobile. According to the total Pb and Zn concentrations, their mobility characteristics and the index of geoaccumulation for all studied soil samples, it is observable that the paddy soil sample from location VII–2 represents a potential environmental risk.

**Key words:** Pb and Zn contamination; paddy fields; sequential extraction procedure; Kočani Field; Macedonia

## INTRODUCTION

An numerous areas of the world soil contamination has become a serious problem. Soil contamination by anthropogenic heavy metals resulting from the application of sewage sludge, fertiliers, industrial historical and recent mining activities is widespread, and extensive investigations have been carried out recently in some countries and regions (Chlopecka et al., 1996; Culbard et al., 1998; Lu et al., 2003; Alloway, 1990; Colbourn & Thornton, 1978; Davies, 1983; Li & Thornton, 1993, 2001; Verner & Ramsey, 1996). The contamination of soils by heavy metals has long term environmental and health implications, because heavy metals are usually persistent in soil and can remain at significant levels for millennia (Mcgrath, 1987). The distribution of heavy metals in soils is influenced by the nature of parent materials, climate and their relative mobility characteristics depending on soil parameters, such as mineralogy, texture and classification of soil (Krishna & Govil, 2007). The bioavailability of heavy metals in soils affects soil quality and its use in food production. Therefore, the assessment of heavy metal contamination in soils is of vital important to the affected areas.

Figures describing the total content of heavy metals in soils present limited information on the mobility and bioavailability of the heavy metals found (Leschber et al., 1985; Kramer & Allen, 1988). They give information concerning possible enrichment of the soil with heavy metals, but the severity of pollution also depends on the proportion of their mobile and bioavailable forms which determines their mobilisation capacity and how they will behave in the environment. Consequently, sequential extraction procedures have been developed to define the amounts and proportions of metals present in different forms of soil: water soluble, exchangeable and carbonate fractions are considered readily mobile and bioavailable, whereas a residual fraction, is considered immobile and may not be expected to be released under natural conditions. The sequential extraction procedure provides information about the differentiation between the relative bonding strengths of metals in

various phases, and about their potential reactivity under different physicochemical environmental conditions. It is considered useful for evaluating mobility and bioavailability of heavy metals in soils (Tessier et al., 1979; Shuman, 1985).

Limited information exists concerning the spatial distribution and availability of heavy metals in soils of the Kočani Field in Macedonia (Dolenec et al., 2007). Soil contamination with heavy metals is due to historical and recent mining operations, the irrigation of paddy fields using acid mine drainage water, the release of untreated mine effluent into riverine water as well as the application of sewage sludge and fertilizers which are growing practices in this area.

In this study, the index of geoaccumulation was used to assess the pollution of the investigated soils and a systematic investigation of the Pb and Zn contamination of surficial soils was carried out using the sequential extraction procedure in order to explore the mobility and potential bioavailability of heavy metals.

## MATERIALS AND METHODS

### *Study area*

Kočani Field lies in the valley of the Bregalnica River, which is situated in eastern Macedonia, about 115 km from the capital city Skopje (Fig. 1). The broader region is well known as an agricultural area (paddy fields), for its thermal waters and for its long mining history dating to the pre–Middle Ages.

The most recent phase of mining began after the Second World War. Several Pb–Zn ore deposits are related to the Tertiary acidic to intermediate volcanogeno-intrusive complexes of the Besna Kobila–Osogovo–Tassos metalogenic zone in the east of the region and the Tertiary volcanogenic complexes of the Lece–Chalkidiki metalogenic zone in the north of Kočani Field (Serafimovski & Aleksandrov, 1995).


**Fig. 1:** Study area, Kočani Field, Macedonia

The Zletovo Pb–Zn deposit lies in the eastern part of the Kratovo–Zletovo volcanogenic complex and occupies the central part of the Kratovo–Zletovo ore district. It is located in the area of the village of Dobrevo, about five kilometres northwest of the Zletovo settlement. The mineral association is comparised of galena (principal ore mineral) and sphalerite, with subordinate pyrite, lesser amounts of siderite, chalcopyrite, pyrhotine, marcasite and magnetite. The Zletovo Mine is active up to the present day with an annual capacity of about 350, 000 tonnes of approximately 8% Pb and Zn concentrate.

The mining activities, the abandoned sites of old mines, the large amounts of untreated waste material and the effluents from the Pb–Zn ore deposit Zletovo have all caused expansion of high heavy metal loads across the entire region. The acid mine waters and the effluents from the ore processing facilities are discharged untreated into the Zletovska and Bregalnica rivers and this represents a further pollution source that could seriously affect the soil as well as the food and feed crops of Kočani Field. Untreated municipal waste and domestic sewage from the cities of Kočani and Orizari are discharged into the Kočanska and Orizarska rivers, which are also used for irrigation purposes, and therefore this represents a potential pollution source for the surrounding paddy fields.

### *Soil sampling and analysis*

The paddy soil of Kočani Field originates from the composite material of the sediment derived from igneous, metamorphic and sedimentary rocks transported by the Bregalnica River and its tributaries and deposited in the Kočani depression (Dolenec et at., 2007).

The sampling of the soil was carried out in autumn 2005 in order to determine the concentration and distribution of the potentially toxic heavy metals, Pb and Zn. The soil was collected from 5 locations (I–3, II–6, III–5, VI–4, and VII–2) across the Kočani paddy fields (Fig. 2).

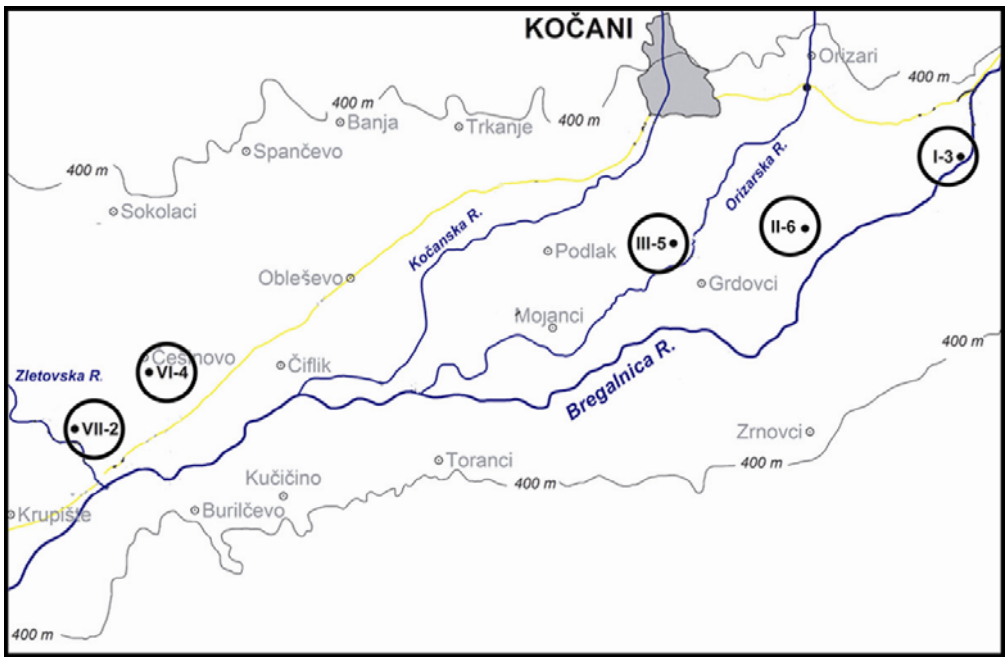


**Fig. 2.** Sampling points located in the study area

Near-surface paddy soils (0–20 cm in depth) were sampled because in agricultural soil it is not possible to distinguish the A, B and C horizons. Each soil sample was made up of a composite of five sub-samples taken from within a 1×1 m square. The soil samples were then air dried at room temperature (about 25 ºC) for one week and sieved through a 2-mm polyethylene sieve to remove plant debris, pebbles and stones. Afterwards the samples were ground in a mechanical agate grinder to a fine powder (< 63<mu>m) for subsequent geochemical analysis.

The paddy soil samples were analyzed for Pb and Zn concentrations in a certified commercial

Canadian laboratory (Acme Analytical Laboratories, Ltd.) after extraction for 1 h with 2-2-2-HCl-$HNO_3$-$H_2O$ at 95 °C by inductively coupled plasma mass spectrometry (ICP-MS). The accuracy and precision of the soil analyses were assessed by using international reference material such as CCRMR SO–1 (soil) and USGS G–1 (granite). The analytical precision and the accuracy were better than ± 5 % for the analyzed elements.

*Sequential extraction procedure*

A sequential extraction procedure, modified method by TESSIER et al. (1979) was applied to study the soil samples. The main purpose of performing a sequential extraction was to investigate the association of chemical elements with a different fractionation in soil through several diverse dissolution steps.

The soil samples weighing 1g were placed in screw-top test tubes. For the sequential leaching procedure, the sample was leached, centrifuged, decanted, washed and then the residue was leached again in a process of five steps moving from the weakest to strongest solution: water → ammonium acetate → sodium pyrophosphate → cold hydroxylamine hydrochloride → hot hydroxylamine hydrochloride. The concentration of Pb and Zn in the solution was then measured by using a Perkin Elan 6000 ICP-MS for the determination of sixty or more elements. QA/QC protocol meant that a sample duplicate was incorporated to monitor analytical precision, and a reagent blank measured background and aliquot of an in-house Reference Material to monitor accuracy. Raw and final data went through a final verification by a British Columbia Certified Assayer.

The sequential extraction method operationally determines Pb and Zn in five different chemical fractions:

– water soluble fraction (distilled water),

– exchangeable and carbonate bound fraction (1 M ammonium acetate),

– organic (oxidizable) fraction (0.1 M sodium pyrophosphate),

– Mn hydroxide (reducible) fraction (cold 0.1 M hydroxylamine hydrochloride) and

– Fe hydroxide (reducible) plus crystalline Mn hydroxide (residual) fraction (hot 0.25 M hydroxylamine hydrochloride).

The highly stable metal forms incorporated into residual fractions are unlikely to be released under weathering conditions. On the other hand, soluble, exchangeable, oxidizable and reducible fractions are quite labile, and hence more accessible to plants and thus the food chain (Kabata-Pendias, 1993).

## RESULTS AND DISCUSSION

*Total heavy metal concentration*

The critical total soil heavy metal concentration is defined as the range of values above which toxicity is considered to be possible. Total heavy metal concentrations of Pb and Zn in the paddy soil samples from Kočani Field together with the assumed permissible level of heavy metals adopted by the National Environmental Protection Agency of Slovenia (Uradni List RS, 1996), the maximum allowable concentrations (MAC) of trace elements in agricultural soil proposed by the German Federal Ministry of Environment (1992) and the critical soil total heavy metal concentration ranges defined by Kabata-Pendias & Pendias (1984) are displayed in Table 1.

Table 1

*Total elemental concentrations in the paddy soil samples of Kočani Field*

| Element | Pb (mg/kg) | Zn (mg/kg) |
|---|---|---|
| Location | | |
| I–3 | 81 | 162 |
| II–6 | 32 | 100 |
| III–5 | 24 | 102 |
| VI–4 | 41 | 105 |
| VII–2 | 892 | 1134 |
| 1 | 100–400 | 70–400 |
| 2 | 85 | 200 |
| 3 | 100 | 200 |

1) Critical soil total concentration ranges given by Kabata-Pendias and Pendias; **2**) limits for elemental concentrations in soil (Environmental Protection Agency of Slovenia (Uradni list RS 1996); **3**) Maximum allowable concentrations (MAC) of trace elements in agricultural soils proposed by the German Federal Ministry of the Environment (1992).

*Lead (Pb)*

Agricultural soils usually include a wide range of Pb content, which depends on a number of factors such as the parent rock material, pedogenic processes and the anthropogenic input from surrounding ecosystems (Adriano, 1986).

The Pb concentrations determined in all paddy soil samples were in a range from 24 to 892 μg $g^{-1}$. The highest Pb concentration (892 μg $g^{-1}$) was measured in a paddy soil sample from location VII–2 and this value is above the limits provided by the environmental protection agencies of Slovenia and Germany (85 μg $g^{-1}$ and 100 μg $g^{-1}$) and the limit values given by Kabata-Pendias & Pendias (1984) (100–400 μg $g^{-1}$) (Table 1). It is also above the median values of Pb content in contaminated agricultural soil reported by Lee et al. (2005) and Liu et al. (2005).

*Zinc (Zn)*

As an average Zn content present in world soils figures showing concentrations of 90 μg $g^{-1}$ have been given by Bowen (1979).

In the present study Zn concentrations in paddy soil samples were in the range of 100–1134 μg $g^{-1}$. Increased concentration of Zn (1134 μg $g^{-1}$, Table 1) was again noticed in the paddy soil sample from VII–2. The Zn concentration in sample VII–2 exceeded all given heavy metal limit values (Table 1).

The data clearly shows that the paddy soil samples from locations I–3, II–6, III–5 and VI–4 contain slightly enhanced Pb and Zn concentrations but that the paddy soil sample from VII–2, located in the vicinity of the Zletovska River is highly impacted by Pb and Zn. The investigated heavy metals are important ore-forming elements in the Pb-Zn polymetallic mineralisation of the Zletovo–Kratovo ore district (Zletovo mine) drained by the Zletovska River (Dolenec et al., 2007). Acid mine water in untreated effluents from Zletovo mine is discharged into the Zletovska River, which is used for the irrigation of the nearby paddy fields. It is therefore the soil sample VII–2 contains such excessively high values of Pb and Zn.

*Index of geoaccumulation*

The index of geoaccumulation ($I_{geo}$) can be used to estimate whether or not soils have been contaminated by heavy metals (Müller, 1969, 1979) : $I_{geo} = \log_2 C_N / 1.5\ B_N$. $C_N$ is measured concentration of element $N$ in soils and $B_N$ is the content of the element $N$ in "average shale" (Turekian & Wedepohl, 1961), either directly measured in texturally equivalent uncontaminated soils or taken from the literature. The factor 1.5 is initiated to include possible differences in the background values due to lithological variations.

The Müller Index of Geoaccumulation, $I_{geo}$, consists of seven grades ranging from unpolluted to very seriously polluted (Table 2). Grade 6 indicates a 64-fold enrichment over the background values (Singh et al., 1997).

Table 2

*Index of geoaccumulation ($I_{geo}$) and contamination level*

| $I_{geo}$ | $I_{geo}$ class | Contamination level |
|---|---|---|
| < 0 | 1 | Uncontaminated |
| 0–1 | 2 | Uncontaminated to moderately contaminated |
| 1–2 | 3 | Moderately polluted |
| 2–3 | 4 | Moderately to highly polluted |
| 3–4 | 5 | Highly polluted |
| 4–5 | 6 | Highly to very highly polluted |
| > 5 | 7 | Very seriously polluted |

In our calculation of $I_{geo}$, $B_N$ is the concentration of studied elements (Pb and Zn) in the earth's crust (Taylor & Mclennan, 1995). The $I_{geo}$ values of Pb and Zn in the studied soils are displayed in Table 3.

Table 3

*The results of the $I_{geo}$ values for the studied soils*

| Soil sample | $I_{geo}$ (Pb) | $I_{geo}$ (Zn) |
|---|---|---|
| I–3 | 2.75 | 0.43 |
| II–6 | 1.42 | –0.26 |
| III–5 | 1 | –0.23 |
| VI–4 | 1.77 | –0.19 |
| VII–2 | 6.21 | 3.24 |

According to the $I_{geo}$ classes the soils from location VII–2 were very seriously polluted with Pb and highly polluted with Zn. The soil samples from other locations were moderately to highly polluted

with Pb and uncontaminated to moderately contaminated with Zn.

*Pb and Zn chemical partitioning*

The water soluble fraction comprises highly mobile and thus potentially bio available metal species. An exchangeable fraction contains weakly bound metal species, that can be released by ion-exchange reaction with cations such as $Ca^{2+}$, $Mg^{2+}$ or $NH_4^+$. The metals present in exchangeable fractions are also accessible for plant uptake and therefore very labile. The oxidisable fraction includes metals bound to organic matter, which can, under oxidising conditions, be released into the surrounding ecosystem. In the reducible fraction the unstable metal forms are connected with amorphous Mn hydroxides and this connection can, under reducing conditions, be easily discharged and approachable for the biota. For the reducible plus residual fraction the metals found were linked to amorphous Fe hydroxides (reducible fraction) and to crystalline Mn hydroxide minerals (residual fraction). Under reducing conditions the metals in a reducible fraction can be expected to be released into nature. The residue was made up of heavy metals defined as being within their crystalline matrix and thus, these metals are not likely to be discharged under normal environmental conditions (Dean, 2007; Filgueiras et al., 2002; Kazi et al., 2002). Figure 3 represents the results of the sequential extraction procedure (heavy metal binding forms).

*Lead (Pb)*

The presence of Pb in extraction fractions of all investigated soil samples was arranged in this way: reducible plus residual > reducible > oxidisable > exchangeable > water soluble fraction. The highest share of Pb in reducible plus residual fraction was detected in the paddy soil sample from location VII–2 (54.46%) and the highest part of Pb in reducible fraction was found in soil sample VI–4 (38.96%) (Fig. 3).

*Zinc (Zn)*

The amount of Zn present in extraction fractions in all samples was arranged in the following order: reducible > reducible plus residual > oxidisable > exchangeable > water soluble fraction. The highest amount of Zn in reducible plus residual and residual fraction phase was determined in the paddy soil sample from sampling site III–5 (49.19% and 36.9%) (Fig. 3).

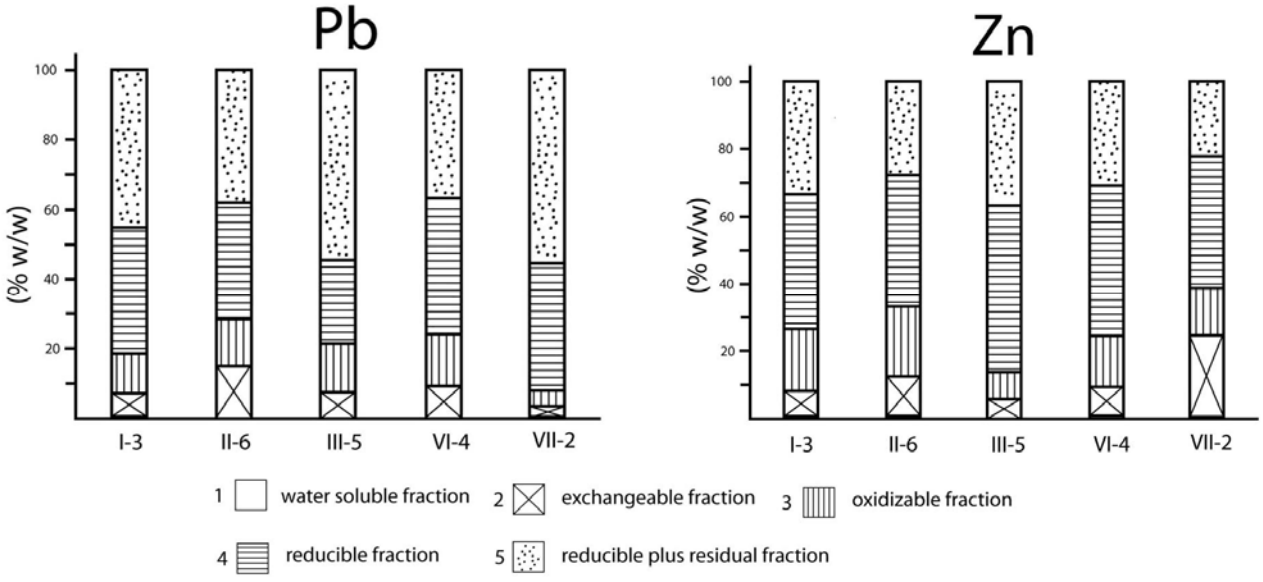


**Fig. 3.** Heavy metal binding forms for Pb and Zn.

A large part of the Pb is defined as non-mobile because of its containment within a cristalline matrix in residual fraction. To some extent Pb was connected with amorphous Mn hydroxides and amorphous Fe hydroxides in reducible fraction. Zn was dominantly associated with amorphous Mn

hydroxides and amorphous Fe hydroxides in reducible fraction as well. For that reason the Pb and Zn are under reduction conditions and therefore very unstable and mobile.

From the environmental and utilisation points of view it is notable that the paddy soil sample from location VII–2 near Zletovska River and Zletovo mine with its highly elevated Pb and Zn concentrations, its rating under the introduced index of geoaccumulation and its mobility characteristics represents a potential risk for surrounding ecosystems.

## CONCLUSIONS

Total Pb and Zn distribution characteristics in paddy soil samples from Kočani Field, Macedonia, were reported. The total amount of Pb and Zn concentration was measured with ICP-EAS, and Pb and Zn binding forms were determined using a sequential extraction procedure.

The results showed that the paddy soil sample (section VII–2) from the western part of Kočani Field in the vicinity of the Zletovska River exhibited very high concentrations of Pb and Zn which significantly exceeds the limits proposed by the Slovenian and German environmental agencies and critical soil total concentration ranges given by Kabata-Pendias and Pendias. Thus, the Pb and Zn surface enrichment in soil sample VII–2 clearly revealed an anthropogenic origin of the pollution.

According to the $I_{geo}$ classes the soils from location VII–2 were very seriously polluted with Pb and highly polluted with Zn.

Pb was dominantly present in reduction and residual fraction, which indicates that some part of the Pb is non-mobile and thus potentially the least harmful. Zn and also part of the Pb were bounded to amorphous Fe and Mn hydroxides in reducible fraction. Therefore, under varied reduction conditions, the mobilisation and release of Zn and Pb from the soils can be expected.

The paddy soil sample from location VII–2 with its highly elevated Pb and Zn concentrations, calculated index of geoaccumulation and their described mobility characteristics represents a potential environmental risk. To assess the possible health risk, more detailed studies on various heavy metal contaminations in surrounding areas are needed.

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Р е з и м е

## ДИСТРИБУЦИЈА НА Pb И Zn И НИВНАТА ФОРМА ВО ОРИЗОВИТЕ ПОЧВИ ВО КОЧАНСКО ПОЛЕ (МАКЕДОНИЈА)

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**Клучни зборови:** Pb и Zn контаминација; оризови полиња; процедура на секвенцијална екстракција; Кочанско Поле; Македонија

Со употреба на процедурата на секвенцијална екстракција беа проучувани дистрибуцијата и хемиските карактеристики на Pb и Zn во оризовите почви во Кочанското Поле, Македонија. Ова проучување беше спроведено со цел да се објасни контаминацијата со метали откриена во оваа област која се должи на историските и современи рударски активности. Во примерокот на оризната почва од локацијата VII–2 во близина на рудникот Злетово, во западниот дел на Кочанско Поле, се откриени силно покачени концентрации на Pb и Zn кои при редукциони услови се многу нестабилни и мобилни. Според вкупните концентрации на Pb и Zn, а со оглед на нивната мобилност и индексот на геоакумулација може да се заклучи дека од сите проучувани примероци почва примерокот од локацијата VII–2 претставува потенцијален ризик за животната средина.